Quantum Monte Carlo for electronic excitations of free-base porphyrin

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Accurate calculations of allowed and non-allowed transitions in porphyrin are reported. Using the quantum Monte Carlo method in the diffusion Monte Carlo variant, the vertical transition between the ground state singlet and the second excited state singlet as well as the adiabatic transition between the ground state and the lowest triplet state have been computed for this 162-electron system. The present theoretical results are compared to experiment and to results of other theoretical methods. The diffusion Monte Carlo energy differences are found to be in excellent agreement with experiment. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1646356]

The porphyrin molecule and its derivatives play an essential role in numerous biological processes including photosynthesis and oxygen transport, and in emerging medical technologies—for example, anti-viral therapeutics. A detailed understanding of the excited states of these systems is essential to elucidating key mechanisms such as oxygen binding and transport, and electron transfer as they occur in biological systems. Despite numerous experimental and *ab initio* theoretical studies, the basic photophysics of porphyrins is not completely understood. For example, recent theoretical studies have proposed reinterpretations of the different features of the spectrum of free base porphyrin (FBP, $C_{20}N_4H_{14}$).

The electronic spectrum of FBP is characterized by three regions: the so-called Q band in the visible region which is relatively weak; the intense B band which occurs in the near UV; and the higher UV bands, N, L and M, which are broader and diffuse. Owing to the inherent sensitivity of the excitation spectra of these systems to structural and chemical changes, it is necessary to employ highly accurate methods in order to make reliable theoretical predictions and to be able to compare directly with experiment. Recently, the quantum Monte Carlo (QMC) approach,[1] which solves the full 3N-dimensional Schroedinger equation directly, has been applied to several large chemical systems.[2]

In the present study, the transition energy between the ground state and lowest excited state of the Q band of FBP was calculated using the DMC method for all electrons of the molecule; effective core potentials were not introduced. A simple method for constructing excited-state trial wave functions has been followed, and its accuracy is compared to alternative approaches and to experiment.

For the DMC approach used in this study,[3] a variational trial wave function was constructed as a product of a Slater determinant of Hartree-Fock orbitals and a correlation function dependent on interparticle distances for both singlet and triplet states. For the triplet excited state, the trial wave function was a restricted-open shell Hartree Fock (ROHF) determinant. For the singlet excited state, we modified the ROHF triplet wave function by altering the spin occupation of the highest occupied molecular orbital (HOMO), which converted the ROHF triplet state, $1\,^3B_{2u}$, into a singlet with the same spatial symmetry, namely, $1\,^1B_{2u}$. We then constructed the proper spin-adapted two-determinant configuration.

The initial geometry was obtained from Sekino and Kobayashi,[4] and was further refined using the B3LYP/DFT[5] method and a 6-311G** basis set[6] using the NWCHEM[7] software package. At the optimized geometry, a trial wave function was constructed by calculating the HF determinant using the cc-pVDZ basis set.[8] A total of 938 contracted Gaussian-type orbitals (GTOs) were used to construct this wave function.

The ground state singlet to second-excited singlet state excitation energies from several theoretical methods as well as experiment are listed in Table I. The DMC value agrees with experiment to within statistical error bars (i.e., 0.1 eV). The MRSDCI results are also in good accord with experiment. Merchán *et al.* have suggested, however, that the latter results arise from a fortuitous cancellation of errors due to the choice of active space.[9] Similarly, Nooijen and Bartlett suggest that there is no reason to expect the MRSDCI results to be converged.[10] Excited-state extensions of DFT, such as time-dependent DFT and DFT-MRCI show good agreement with experiment.

Results for the lowest triplet excitation energy are also listed in Table I. Nooijen and Bartlett suggest that the low-

TABLE I. Excitation energies (eV) from the ground state to the $1\ ^1B_{2u}$ and $1\ ^3B_{2u}$ states of FBP. Empty slots indicate the absence of data.

Method	Vertical excitation (eV) $1\ ^1B_{2u}$	Vertical excitation (eV) $1\ ^3B_{2u}$	Adiabatic energy difference (eV) $1\ ^3B_{2u}$
CIS[a]	2.66	1.23	
SAC-CI[b]	2.25		
CASPT2[c]	2.26	1.37	
TD-DFT[d]	2.39		
DFT-MRCI[e]	2.38		
MRSDCI[f]	2.40	1.65	
STEOM-CCSD(T)[g]	2.40	1.20	
DMC (This work)	2.45(8)		1.60(10)[k]
Experimental results			
Vapor phase[h]	2.42		
Supersonic jet[i]	2.46		
Frozen solvent[j]			1.58

[a]Reference 15.
[b]Reference 16.
[c]Reference 9.
[d]Reference 17.
[e]Reference 18.
[f]Reference 19.
[g]$1\ ^1B_{2u}$: Ref. 14, $1\ ^3B_{2u}$: Ref. 10.
[h]Reference 12.
[i]Reference 11.
[j]Reference 13.
[k]Calculation performed at the minimum geometry of the B3LYP potential energy surface.

lying triplet states of FBP pose a serious challenge for correlated treatments.[10] For this energy difference, the DMC results are found again to agree with the experimental excitation energy to within the error bars.

To obtain a clear picture of the present findings, laser-induced fluorescence excitation spectroscopy data[11] and Q_y absorption band data from vapor absorption spectra experiments[12] are listed for comparison with theoretical results. The experimental phosphorescence peak associated with the adiabatic singlet-triplet energy difference is taken from the spectrum of Gouterman and Khalil obtained in a frozen solvent at 77 K.[13]

In order to make accurate comparisons with experiment, the all-electron (AE) DMC computations were carried out for sufficiently long simulation to yield statistical error bars of 1 kcal/mol. A small time step of 0.001 a. u. was used to avoid zero time step extrapolation and to achieve a high acceptance ratio for the three states of interest.

The present and other theoretically determined ground state total energies are summarized in Table II. The computed AE-DMC excited state energies are $-988.837(3)$ ($1\ ^3B_{2u}$) and $-988.806(1)$ a.u. ($1\ ^1B_{2u}$). The same computer time was used for the calculation of both states which implies comparable quality of the $1\ ^1B_{2u}$ and $^3B_{2u}$ trial wave functions.

The computer time for the calculations performed in this study was approximately 40 000 CPU hours of IBM SP POWER3+ for each state. Specifically, the calculation was approximately divided into 26 twelve-hour runs, each using 128 processors.

TABLE II. Total energies for ground state FBP from different *ab initio* methods (in a.u.).

Method	Energy
Hartree-Fock	-983.3333[a], -983.430[b]
RASSCF	-983.2138[c]
CCSD(T)	-986.688[b]
DMC	$-988.985(3)$[a]

[a]This work.
[b]Reference 14.
[c]Reference 9.

The present results confirm that DMC can be used to calculate excited state energies for porphyrin that agree to within 0.1 eV of experiment—an accuracy not achieved previously by other computational methods. In addition, the present all-electron total energies are lower in comparison to previously reported CCSD(T) results,[14] implying the recovery of more correlation energy. These results demonstrate the capability of DMC to produce accurate excited-state energies for large (biological and other) molecules where chemical accuracy is required.

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[1] D. M. Ceperley and B. J. Alder, Science **231**, 555 (1986).
[2] A. Luchow and J. B. Anderson, Annu. Rev. Phys. Chem. **51**, 501 (2000).
[3] B. L. Hammond, W. A. Lester, Jr., and P. J. Reynolds, *Monte Carlo Methods in Ab Initio Quantum Chemistry* (World Scientific, Singapore, 1994).
[4] H. Sekino and H. Kobayashi, J. Chem. Phys. **75**, 3477 (1981).
[5] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
[6] R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, J. Chem. Phys. **72**, 650 (1980).
[7] NWCHEM, High Performance Computational Chemistry Group, A Computational Chemistry Package for Parallel Computers, Version 4.1 (2002) (Pacific Northwest National Laboratory, Richland, Washington 99352).
[8] Please supply reference.
[9] M. Merchan, E. Orti, and B. O. Roos, Chem. Phys. Lett. **226**, 27 (1994).
[10] M. Nooijen and R. J. Bartlett, J. Chem. Phys. **106**, 6449 (1997).
[11] U. Even and J. Jortner, J. Chem. Phys. **77**, 4391 (1982).
[12] L. Edwards and D. H. Dolphin, J. Mol. Spectrosc. **38**, 16 (1971).
[13] M. Gouterman and G. Khalil, J. Mol. Spectrosc. **53**, 88 (1974).
[14] S. R. Gwaltney and R. J. Bartlett, J. Chem. Phys. **108**, 6790 (1998).
[15] J. B. Foresman, M. Head-Gordon, J. A. Pople, and M. J. Frisch, J. Phys. Chem. **96**, 135 (1992).
[16] H. Nakatsuji, J. Hasegawa, and M. Hada, J. Chem. Phys. **104**, 2321 (1995).
[17] D. Sundholm, Phys. Chem. Chem. Phys. **2**, 2275 (2000).
[18] A. B. J. Parusel and S. J. Grimme, Porphyrins Phtalocyanines **5**, 225 (2001).
[19] Y. Yamamoto, T. Noro, and K. Ohno, Int. J. Quantum Chem. **42**, 1563 (1992).